

Solid-phase extraction of plutonium in various oxidation states from simulated groundwater using *N*-benzoylphenylhydroxylamine

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Abstract Solid-phase extraction of plutonium in different individual and mixed oxidation states from simulated groundwater (pH 8.5) was studied. The extraction of plutonium species was carried out in a dynamic mode using DIAPAK C16 cartridges modified by *N*-benzoylphenylhydroxylamine (BPHA). It was shown that the extent of recovery depends on the oxidation state of plutonium. The extraction of Pu(IV) was at the level of 98–99% regardless of the volume and flow-rate of the sample solution. Pu(V) was extracted by 90–95% and 75–80% from 10- and 100-mL aliquots of the samples, respectively, whereas the extraction of Pu(VI) did not exceed 45–50%. An equimolar mixture of Pu(IV), Pu(V), and Pu(VI) was extracted by 74%. The distribution coefficients (K_d) and kinetic exchange capacities (S) of plutonium in various oxidation states were measured. It was found that during the sorption process, Pu(V) was reduced to Pu(IV) by 80–90% after an hour-long contact with the solid phase. Pu(VI) is reduced to Pu(V) by 34% and to Pu(IV) by 55%. In the case of mixed-valent solution of plutonium, only Pu(V) and Pu(IV) were found in the effluents.

Keywords Solid-phase extraction · Plutonium · *N*-benzoylphenylhydroxylamine · Groundwater

Introduction

Among the radionuclides present in radioactive wastes, there are a certain number of fission products and minor actinides. Actinides and particularly long-lived isotopes of plutonium are mainly responsible for the environmental hazard. Extensive studies during the last decades have shown that under the natural conditions Pu can be simultaneously stabilized in four oxidation states: +3, +4, +5, and +6. Pu(III) and Pu(IV) are more stable in acidic media, while the higher oxidation states are predominant in the solutions with pH ≥ 7 . At certain concentrations at pH 2–3 Pu(IV) has a strong tendency to hydrolysis, giving rise to the formation of polymeric species [1].

For risk assessment, monitoring of plutonium concentration in contaminated zones is required. Several methods are frequently used for the determination of plutonium speciation in different environmental samples [2, 3]. Apart from liquid–liquid extraction based on a different complexation of various oxidation states of plutonium with various extraction agents, solid-phase extraction (SPE) methods are also fairly effective for the purpose of plutonium speciation [4]. Of a range of chelating reagents available for the SPE of metal ions, benzoylphenylhydroxylamine (BPHA) appears to be one of the most efficient reagents. Being a typical chelating reagent with a rigid bidentate O,O-chelating group [5–7], BPHA has also found application for plutonium recovery from acidic solutions by liquid–liquid extraction [8].

Likewise, SPE on C16 cartridges modified with BPHA has already been demonstrated to be effective for Np(V), Pu(IV), and Am(III) extraction from simulated groundwater solutions and surface water taken from the region of Product Association “Mayak” [9]. This provided us with an impetus that using a similar SPE hardware, plutonium in

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its various oxidation states could also be subject to selective extraction.

Experimental

Chemicals and reagents

Stock solutions of ^{239}Pu (^{241}Am content did not exceed 0.1% w/v) in oxidation states +4, +5, and +6 were prepared using the following methods. Pu(IV) was obtained by electrochemical oxidation of Pu(III) in a hydrochloric acid solution prepared by dissolving a known amount of metallic plutonium in 6 M HCl, using a platinum anode at a potential of 1.2 V. Pu(VI) was prepared by the oxidation of tetravalent plutonium in a hot perchloric acid solution followed by evaporation till a wet-salt state. Subsequently, the dry residue was dissolved in water and the resultant solution was evaporated several times. Pu(V) solution was obtained by reducing Pu(VI) in a solution with pH 2 using hydrogen peroxide. Plutonium concentrations in the stock solutions were $(5\text{--}10) \times 10^{-3}$ M. Working solutions were prepared by dilution of stock solutions with the required volume of SGW having the following composition (in g/10 L): Na_2CO_3 —0.276, CaCl_2 —0.079, AlCl_3 —0.00047, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ —0.279, NaHCO_3 —2.483, Na_2SO_4 —0.185, NaCl —0.176, KCl —0.045; pH 8.5. Aliquots of the individual solutions of Pu(IV), Pu(V), and Pu(VI) were introduced into 100 mL SGW and a mixed solution pH was adjusted and Eh was measured. All chemicals used were of analytical grade.

Instrumentation

Plutonium species in the solutions obtained were monitored using spectrophotometers “Unicam UV-300” and “Cary 100”.

Hydrolyzed and polymerized forms of plutonium were identified by ultrafiltration at 14,000 rpm. using a “SM-50” centrifuge. Separation of particles with molecular masses of 30 kDa and larger was performed by centrifugation during 30 min by use of filters with 3 nm pore sizes. Concentration of ionic and polymeric forms of plutonium was estimated from a difference in plutonium concentrations before and after ultrafiltration. DIAPAK C16 cartridges purchased from BioChimMak, MSU (Moscow State University, Russia) were applied to the investigation of plutonium speciation. It is a silica material chemically modified with hexadecyl groups ($\text{SiO}_2\text{--OSi--}(\text{CH}_3)_2\text{C}_{16}\text{H}_{33}$) having an average pore size of 130 nm, the specific surface area of $300 \pm 30 \text{ m}^2$ per g and size distribution in the range of 50–160 μm .

Each cartridge was conditioned by flushing with 5 mL ethanol and then modified by passing through 10 mL of 0.2 M BPHA in ethanol. The sorption of plutonium was

studied under dynamic conditions by passing the Pu-containing solutions through the cartridge at a flow-rate of 1 mL/min. 10 mL aliquots of the filtrate were collected after certain time intervals to monitor the variation in plutonium concentration. After the sorption equilibrium was achieved, plutonium was desorbed by 0.1 M HNO_3 and the mixed acids solution of 0.35 M HNO_3 + 0.01 M HF was studied.

Liquid–liquid extraction with a 0.2 M 2-thenoyltrifluoroacetone (TTA) solution in toluene was additionally used to estimate the Pu speciation in the effluent after desorption. After the separation of aqueous and organic phases, the plutonium concentrations in each phase were determined, as described below.

Alpha-spectrometry was employed for the determination of plutonium concentration. An aliquot of the test solution was evaporated to dryness on polished stainless-steel targets ($d = 30 \text{ mm}$), following by the target calcination at about 500 °C. Alpha-spectra were acquired using an “Alpha Analyst” spectrometer (Canberra, USA). For pH measurements a pH-meter “Mettler Toledo” MP230 equipped with a combined glass electrode (Hanna Instrument HI 1131B) was used. The electrode was regularly calibrated with respect to pH-buffer standards (pH 1–13; Merck, Darmstadt, Germany). In SPE experiments, the required pH was adjusted with solutions 0.1 M NaOH or 0.1 M HClO_4 . Monitoring of redox potentials (Eh) was performed by a platinum grid using the Ag/AgCl electrode as a reference one.

The dynamic capacity (S , M/g) and the distribution coefficients (K_d , mL/g) were calculated from the following equations:

$$S = (C_0 - C_e) \times V/m \quad (1)$$

$$K_d = S \times 1000/C_e \quad (2)$$

where C_0 is the initial concentration of plutonium in the solution (M), C_e is the plutonium concentration in the ultra filtrate (M), V (mL), and m is the mass of the sorbent (g).

Results and discussion

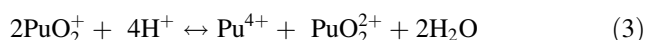
Characteristics of initial SGW solutions of plutonium in various oxidation states used in this study are presented in Table 1. As can be seen, the higher the redox potential of the solution, the higher oxidation state of plutonium is stabilized. This observation is in agreement with the data of Choppin et al. [10]. After ultrafiltration, the plutonium concentration in the filtrate corresponds to the concentration of its ionic forms and the quantity of Pu retained by the filter is in accordance with the concentration of its polymeric forms. Under the present conditions, Pu(IV) hydrolyses results in the formation of polymeric species that was

Table 1 Speciation of Pu in the initial SGW solutions

Pu oxidation state	[Pu] _{tot} (M)	pH	Eh (mV)	[Pu] _{filtrate} (M)	Ratio of ionic form (%)
Pu(IV)	6.05×10^{-6}	8.76	356	4.84×10^{-7}	8.0
Pu(V)	4.23×10^{-6}	8.61	406	3.76×10^{-6}	88.9
Pu(VI)	6.22×10^{-6}	8.27	582	5.97×10^{-6}	99.0
Pu mixture	7.27×10^{-6}	8.45	532	4.42×10^{-6}	60.8

confirmed by the results of ultrafiltration experiments. It was shown that nearly 92% of tetravalent plutonium in the solutions occurs in polymeric forms.

89% Pu(V) presents in ionic forms and the rest 11% as polymeric forms. This can be due to the disproportion of Pu(V) according to reaction 3:



As a result, some amount of Pu(IV) is produced, which then undergoes polymerization, whereas 99% of Pu(VI) remains in the ionic forms.

In order to estimate the reciprocal influence of different oxidation states of Pu on its sorption from the solution containing all three forms, Pu(IV), Pu(V), and Pu(VI), at equal concentration ratios was studied.

Results of SPE experiments are shown in Fig. 1 in the form of dependences of Pu ratios (in %) remained in the effluent after passing of Pu(IV), Pu(V), and Pu(VI) and the mixed-valent Pu solution through the SPE cartridge modified by BPHA.

As one can see, the SPE behavior of plutonium in various oxidation states differs rather considerably. The polymerized forms of Pu(IV) are sorbed rather effectively

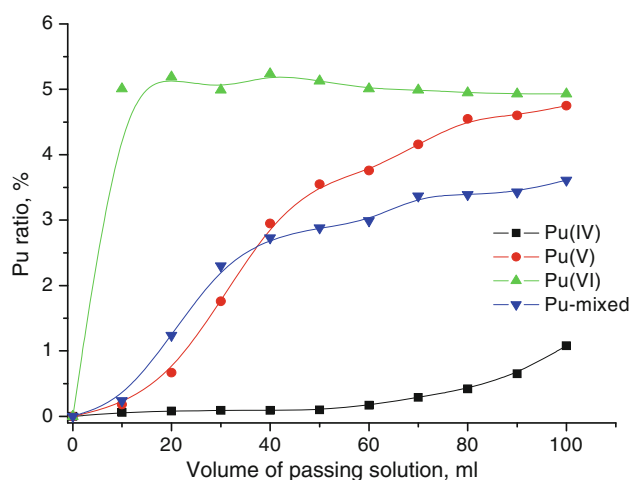
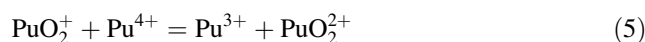


Fig. 1 The ratios of Pu(IV), Pu(V), Pu(VI) and mixed-valent Pu obtained after passing through the cartridge modified by BPHA

during passing the first 50 mL of the solution, that is due to a high sorption affinity of polymeric plutonium macromolecules [11–13]. Further passing the solution results in an increase of plutonium concentration in the effluent that may be attributed to the reduction of Pu(IV) to Pu(III) under the action of BPHA, as reported in [8], or to plutonium disproportionation [14]:



Because the disproportionation may take place according to reactions 4–6, Pu(III), Pu(V), and Pu(VI) can be found in the equilibrium solution. In these oxidation states Pu is less inclined to sorption, while the extent of Pu(IV) extraction under these conditions reaches 97%.

The behavior of Pu(V) is completely different. Its concentration, after the elution of the first 5–10 mL, changes only slightly since the polymeric Pu(IV) comprises about 11% of total Pu. Upon passing the following 30 mL, a sharp increase in the plutonium concentration in the eluate is observed. A further concentration increase is also controlled either by reduction or disproportionation [see reaction 3]. It was also found that the Pu(V) sorption depends on the volume of the solution passed through the cartridge or, in other words, on the time of contact of the solution with the SPE material. The Pu sorption changes from 85–90% when 10 mL of the solution has been passed to 75–78% for 100 mL (i.e. 10 and 100 min, respectively). This observation is in agreement with the Pu(V) disproportionation, being the second-order reaction for plutonium cations.

The sorption rate of Pu(VI) seems to be constant upon passing the whole volume of the solution, reaching a plateau after loading 10 mL. Pu(VI) is sorbed by about 50% in case of a 100-mL sample under these conditions.

The mixed-valent plutonium species sorbed by 74%.

The exchange capacities and distribution coefficients for Pu(IV), Pu(V), and Pu(VI), as well as of mixed-valent plutonium forms are listed in Table 2. It can be seen that the exchange capacity of plutonium ions in all the oxidation states do not decrease much with increasing the solution volume passed through the cartridge.

The distribution coefficients of plutonium significantly depending on the oxidation states and the volume of solution passed through the cartridge. The K_d for Pu(IV) sorbed from the first 20–25 mL is relatively high, 2,700–2,000 mL/g. For Pu(IV) a rather complicated dependence of K_d on the volume of solution was obtained. This might be due to either the reduction of Pu(IV) to Pu(III), or to Pu(IV) disproportionation and formation of

Table 2 Exchange capacities and distribution coefficients of Pu(IV), Pu(V), Pu(VI), and mixed-valent plutonium species as a function of the volume of solution passed through the sorbent

V (mL)	Pu(IV)		Pu(V)		Pu(VI)		Pu mixed	
	<i>S</i> (M/g)	<i>K_d</i> (mL/g)	<i>S</i> (M/g)	<i>K_d</i> (mL/g)	<i>S</i> (M/g)	<i>K_d</i> (mL/g)	<i>S</i> (M/g)	<i>K_d</i> (mL/g)
10	1.00×10^{-4}	2,749	6.92×10^{-5}	901	5.16×10^{-5}	17	1.18×10^{-4}	686
20	1.00×10^{-4}	2,084	6.57×10^{-5}	229	4.97×10^{-5}	15	1.06×10^{-4}	117
30	1.00×10^{-4}	1,913	5.80×10^{-5}	77	5.19×10^{-5}	17	9.33×10^{-5}	56
40	9.99×10^{-5}	1,749	4.95×10^{-5}	39	4.92×10^{-5}	15	8.81×10^{-5}	44
50	9.98×10^{-5}	1,595	4.53×10^{-5}	30	5.03×10^{-5}	16	8.62×10^{-5}	41
60	9.92×10^{-5}	989	4.38×10^{-5}	27	5.16×10^{-5}	17	8.49×10^{-5}	39
70	9.79×10^{-5}	552	4.10×10^{-5}	23	5.18×10^{-5}	17	8.03×10^{-5}	33
80	9.65×10^{-5}	375	3.82×10^{-5}	20	5.23×10^{-5}	17	8.01×10^{-5}	32
90	9.42×10^{-5}	238	3.78×10^{-5}	19	5.24×10^{-5}	17	7.96×10^{-5}	32
100	8.99×10^{-5}	138	3.68×10^{-5}	18	5.25×10^{-5}	17	7.74×10^{-5}	29

Pu(III), Pu(V), and Pu(VI) that causes a lower plutonium sorption.

The distribution coefficient for Pu(V) decreases drastically when passing the first 30 mL of the solution, and then levels-off after passing 40 mL. The initial decreasing may be explained by disproportionation or reduction of Pu(V) to Pu(IV). The same trend was observed for the mixed-valent plutonium solution. In contrast to other oxidation states, the distribution coefficient for Pu(VI) remains virtually unchanged within the whole sorption procedure (up to 100 mL of the passed solution).

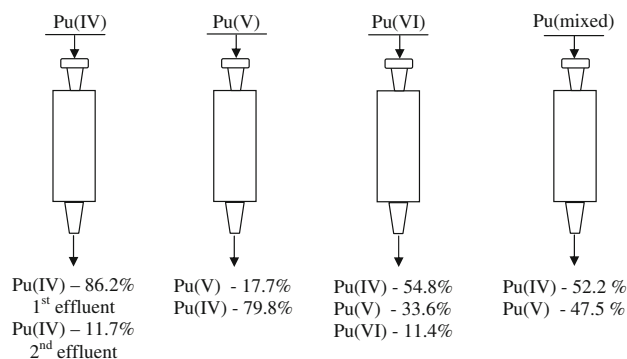
The oxidation states of plutonium existing in the sorption process were identified using spectrophotometric studies. The molar absorptivities (ϵ) were preliminarily calculated from the absorption spectra of Pu solutions (in SGW) in a specified oxidation state at the known plutonium concentration. The values of (ϵ), as well as the wavelength of maximum plutonium absorption (λ) and absorbance (*D*) are given in Table 3.

100 mL portions of the prepared solutions were passed through the modified cartridges and then plutonium was eluted using a mixed solution of acids 0.35 M HNO₃ + 0.01 M HF. If complete plutonium desorption was not reached, the mixed solution of acids 1.0 M HNO₃ + 0.01 M HF was used. It was supposed that during the sorption the plutonium oxidation state does not change. The volume of acids taken for desorption was equal to 10 mL hereby tenfold plutonium concentration was reached. After the desorption of Pu from the column was completed, the absorption spectra of the effluents were recorded. The concentration of each oxidized form of plutonium was determined using corresponding absorptivities found earlier.

Figure 2 represents the plutonium oxidation states distribution after the sorption onto BPHA. During the desorption of Pu(IV), 86.2% of plutonium came out of the

Table 3 Extinction coefficients of Pu(IV), Pu(V) and Pu(VI) in SGW

Oxidation state of Pu	[Pu] (M)	λ (nm)	<i>D</i>	ϵ (M ⁻¹ cm ⁻¹)
Pu(IV)	9.72×10^{-5}	477	2.7×10^{-3}	27.8
Pu(V)	9.46×10^{-5}	569	1.2×10^{-3}	12.68
Pu(VI)	1.04×10^{-4}	831	1.4×10^{-2}	134.00

**Fig. 2** The plutonium speciation during the sorption onto BPHA (100% corresponds to the total content of Pu in the respective eluent)

cartridge within passing the first 5 mL of 0.35 M HNO₃ + 0.01 M HF eluent. An additional 5-mL portion almost completes the recovery of the residual Pu(IV). Pu(V) was fully eluted by 10 mL of 0.35 M HNO₃ + 0.01 M HF solution. The absorption spectra have shown up to 80% of Pu to be present as Pu(IV) (the absorption band at 477 nm), and the rest exists as Pu(V) (the absorption band at 569 nm). These data are consistent with the suggestion that Pu(V) is reduced by BPHA during the sorption. Pu(VI) was also shown to be partially reduced in the cartridge: the effluent contained simultaneously Pu(IV),

Table 4 Plutonium extraction by 0.2 M TTA solution in toluene from the SPE eluate. ($V = 10$ mL, $m_{\text{sorbent}} = 100$ mg, $[\text{Pu(V)}] = 1.9 \times 10^{-10}$ M)

Contact time of sorbent with solution, min	5	10	30	60
Content of Pu(V) in the eluate, %	97	88	44	10

Pu(V), and Pu(VI). This explains the low efficiency of sorption of the hexavalent plutonium from SGW solutions. Mainly tetravalent plutonium is extracted during the sorption process. The eluate obtained by the desorption of mixed-valent plutonium consists of only Pu(IV) and Pu(V). Probably, Pu(VI) is reduced to Pu(V) or takes part in the following reaction:



As a result, a higher amount of Pu(V) is obtained compared to the initial solution composition.

Liquid–liquid extraction with TTA was additionally used to estimate the Pu speciation in the eluate after desorption. By varying the time of contact of the test solution with the sorbent, the kinetics of reduction of Pu(V) was estimated. The results of this experiment are represented in Table 4.

As can be seen, after an hour contact with the sorbent up to 90% of Pu(V) is reduced to Pu(IV). Experiments with ^{238}Pu allowed one to deal with the trace concentrations of plutonium were in a rather good agreement with the experiment under dynamic conditions, where a plutonium concentration of 7.93×10^{-6} M was used: the Pu sorption up to 85% was demonstrated. After desorption by 5.0 mL of 0.1 M HNO_3 solution, 60.7% of plutonium was found in the eluate. Further assessment of the speciation of Pu in the eluate showed that it contains 88% of Pu(V) and 10% of Pu(IV). The following elution with a 5-mL portion of 0.35 M $\text{HNO}_3 + 0.01$ M solution recovered the residual plutonium completely. This second portion of the eluate contained 25.7% of the total amount of the sorbed plutonium in which 2% of Pu(V) and 97% of Pu(IV) were determined.

Conclusions

The experiments showed the feasibility of using DIAPAK C16 cartridges modified by BPHA to extract plutonium in various oxidation states from simulated groundwater solutions within a pH range of 7–9. The sorption degree depends on the plutonium oxidation state. Pu(IV) is extracted by 98–99% regardless of the volume and the flow-rate of passing the solutions under study. Pu(V) is extracted by 90–95% from 10 mL of SGW (the contact time is 10 min) and by 75–80% from 100 mL of SGW (the contact time is 100 min). Up to 50% of Pu(VI) retains on

the SPE cartridge from 100 mL of SGW. About 74% of plutonium can be extracted from 100 mL of SGW solution containing the equal concentrations of Pu(IV), Pu(V), and Pu(VI).

Kinetic exchange capacities of plutonium in all the oxidation states do not change considerably during the sorption process. On the other hand, the distribution coefficient varies depending on the plutonium speciation.

During an hour sorption, 80–90% of Pu(V) is reduced to Pu(IV). Pu(VI) is reduced to Pu(V) and Pu(IV) by 34 and 55%, respectively. The sorption of mixed-valent plutonium resulted in the formation of Pu(V) and Pu(IV) under the equilibrium conditions.

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